

Morphology and toughening behaviour of diallyl isophthalate resin/polyarylate alloy

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The excessively brittle diallyl isophthalate (DAIP) resin was toughened using polyarylate (PAR). The cure kinetics and appropriate cure condition were investigated with differential scanning calorimetry. Fracture surfaces showed that phase separation occurred, resulting in a two-phase morphology. At 2 and 5 phr of PAR, spherical particles of PAR containing DAIP inclusions were obtained. Observation of tails at the rear of particles on the fracture surfaces provides some evidence for crack pinning, which resulted in a slight increase in fracture toughness. At 10 phr of PAR a co-continuous connected globular morphology was obtained, leading to a step increase in the fracture toughness by ductile drawing of the PAR. Co-continuous structure was also observed at 15 phr of PAR, and fracture toughness was increased by 1.5 times with little sacrifice in other mechanical properties. From optical and scanning electron microscopy studies on fracture surfaces, the toughening mechanism is considered to be crack path deflection and ductile drawing of PAR. Copyright © 1996 Elsevier Science Ltd.

(Keywords: diallyl isophthalate resin; polyarylate; toughening)

INTRODUCTION

Diallyl isophthalate (DAIP) resins are highly crosslinked thermoset materials that find widespread use in thermoset-reinforced plastics, moulding compounds and electronic connectors due to their outstanding heat resistance, dimensional stability and electrical properties¹. They also have high moisture resistance, so that DAIP/epoxy interpenetrating networks or flexibilized DAIPs are used as a replacement for moisture-sensitive epoxies^{2,3}. In spite of these excellent properties, DAIP resins are extremely brittle because of their high crosslink density and three-dimensional network structure.

To improve their mechanical properties, DAIPs have been co-cured with vinyl monomers having long alkyl chains⁴ and with reactive oligomers⁵. Increased elongation and fracture energy were found with increasing comonomer concentration; however, other mechanical properties such as tensile strength and modulus decreased markedly.

According to recent research, incorporation of tough, ductile and thermally stable engineering thermoplastics [such as poly(ether imide), polysulfone and poly(ether sulfone)] is effective in toughening of highly crosslinked thermosets without sacrificing other desirable mechanical properties^{6–8}. Moreover, as the crosslink density of the thermoset increases, thermoplastic inclusions contribute more to toughening than do soft inclusions. The reason is that soft inclusions are no longer able to induce

energy dissipation when the resin is too highly crosslinked to deform plastically.

In this work, polyarylate (PAR) was used to toughen the excessively brittle DAIP resin. PAR displays excellent thermal resistance and toughness, combined with clarity and ultraviolet stability. Miscibility between DAIP and PAR was predicted from their similar isophthaloyl structures and the small difference in their solubility parameters. In this paper, cure characteristics, morphological changes and mechanical properties of the DAIP/PAR alloy are investigated and possible toughening mechanisms are studied.

EXPERIMENTAL

Materials and sample preparation

Commercial grade DAIP (Daiso Co.) was passed through a neutral alumina column before use. PAR (Unitika Co., U-100; $\bar{M}_n = 21\,200$, $\bar{M}_w = 51\,400$) was dried *in vacuo* at 80°C for at least 12 h. Methylene chloride was used without further purification. The amount of PAR added to the DAIP resin was varied from 0 to 15 phr, samples being prepared by the following procedure. PAR was dissolved in methylene chloride and mixed with DAIP monomer at room temperature. The solution was heated in an oil bath for 1 h at 120°C to drive off methylene chloride. After methylene chloride was removed, the solution became a visually clear, homogeneous and viscous liquid. Then the solution was cooled to 60°C and dicumyl peroxide (DCP) was added with stirring for about 20 min;

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the DCP content was varied from 1 to 4 wt%. After degassing under vacuum at 40°C for 30 min, the resin was poured into a Teflon-coated mould and cured for 8 h at 120°C, 2 h at 140°C, and 2 h at 170°C. Finally, the cured sheet was allowed to cool to room temperature.

Thermal analysis

The optimum amount of DCP and the cure condition for complete reaction of DAIP were determined by differential scanning calorimetry (d.s.c.: Perkin-Elmer DSC7). The conversion was obtained from the area of exotherm peaks during the d.s.c. heating run at 10°C min⁻¹ on the basis that the total heat of reaction of DAIP is 634.4 J g⁻¹ (ref. 9). Isothermal curing at various temperatures was also carried out to determine cure kinetics. The conversion of neat DAIP resin and PAr-modified DAIP resin as a function of time was estimated by the residual exotherm.

Dynamic mechanical measurements at 1 Hz were made in the single cantilever bending mode between 50 and 350°C with a heating rate of 3°C min⁻¹ using dynamic mechanical thermal analysis (d.m.t.a.; Polymer Laboratories MK-II instrument).

Mechanical property measurements

Fracture toughness was measured according to ASTM E399. The critical plane-strain stress intensity factor, K_{IC} , was determined using a single-edge notched specimen (3 mm × 6 mm × 35 mm) in a three-point bending geometry (SN-3PB). The sample was first notched with a saw, and then a razor blade was inserted into the notch and struck to propagate a sharp crack. The precracked specimen was placed in a universal testing machine (Instron 4206) and tested at a crosshead speed of 1.28 mm min⁻¹. Flexural properties were measured on unnotched specimens (3 mm × 12 mm × 60 mm) with a span of 48 mm according to ASTM D790. The mechanical property values reported are the average of at least six tests.

Fractography

The double-notched four-point bending (DN-4PB) technique, which is known to be effective in elucidating the toughening mechanisms of polymer alloys, was used to generate a sub-critically propagated crack¹⁰. For the DN-4PB experiments, cured sheets of PAr-modified DAIP resin were machined into bars with dimensions of 3 mm × 60 mm × 50 mm. These bars were then notched using the same method as for the SN-3PB test, and tested with a crosshead speed of 1.28 mm min⁻¹.

The damage zone around the surviving crack was micro-polished and examined by transmission optical microscopy (TOM; Carl Zeiss, Axioplan). Fracture surfaces were coated with gold and examined by scanning electron microscopy (SEM; Hitachi S-570). When solvent etching of the fracture surfaces was required, specimens were immersed in methylene chloride at room temperature for 24 h before applying the coating.

RESULTS

Cure kinetics

Allyl compounds polymerize with difficulty and yield polymers of low molecular weight. Barlett and Altschul¹¹

Table 1 Conversion of DAIP as a function of DCP content

DCP (wt%)	ΔH (J g ⁻¹)	Conversion (%)
1	-354.4	56
2	-550.3	87
3	-582.7	92
4	-622.1	98

Heat of polymerization of the allyl group is 634.4 J g⁻¹ (ref. 9)

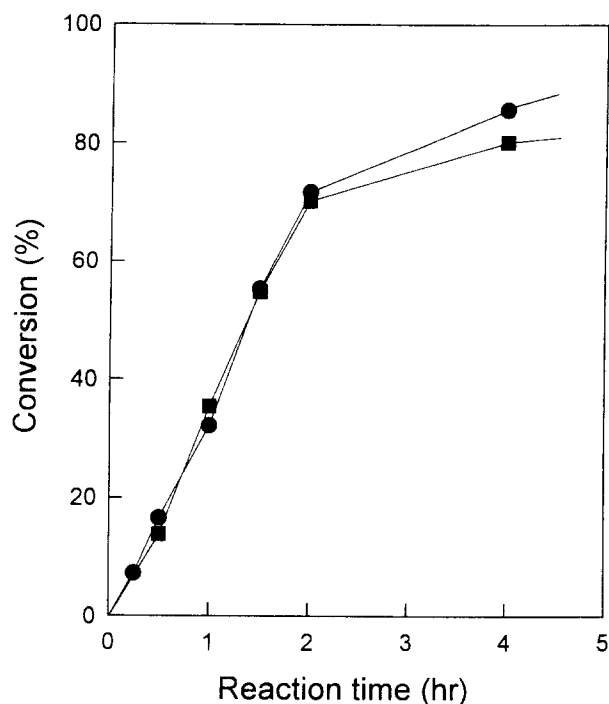


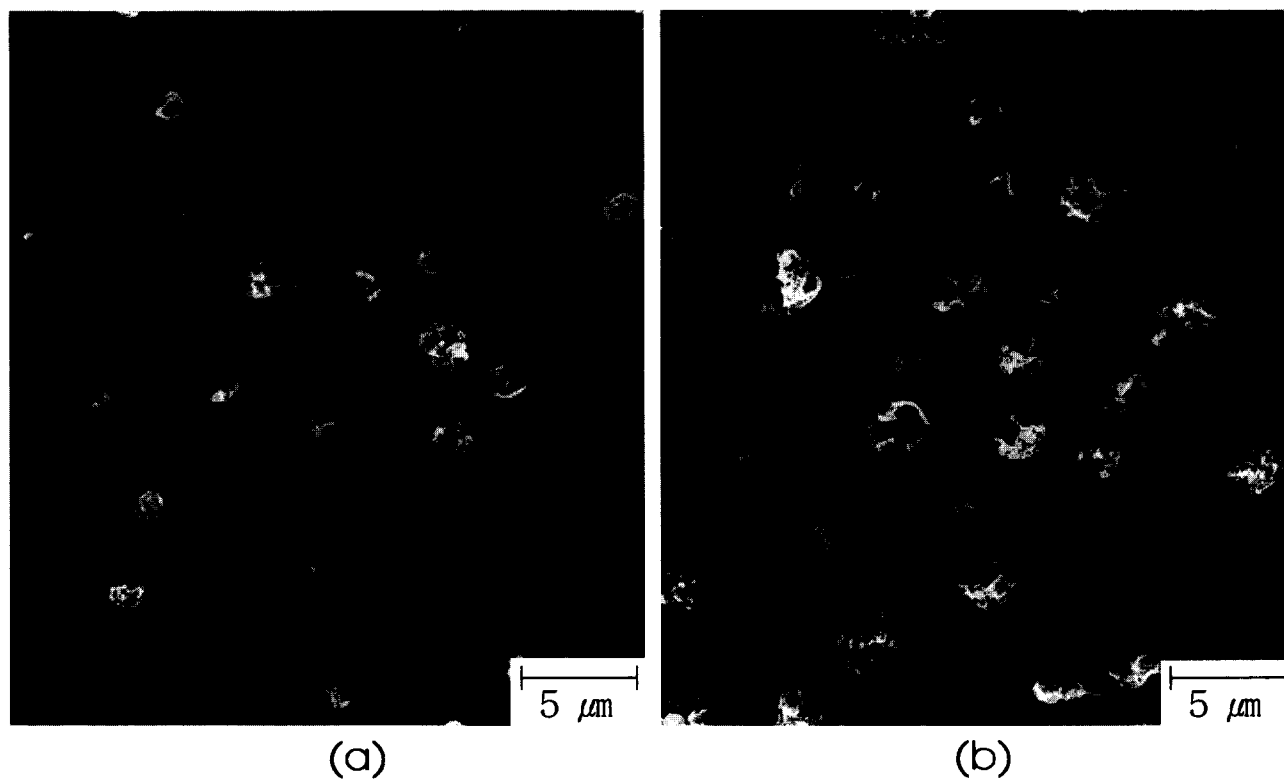
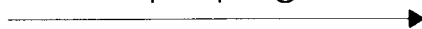
Figure 1 Conversion of the neat DAIP and PAr-modified DAIP as a function of reaction time: ●, neat DAIP; ■, PAr-modified DAIP

have shown that these results can be attributed to degradative chain transfer of allylic hydrogen. Furthermore, a large amount of initiator is required compared with vinyl polymerization. In this work, the optimum content of DCP was determined from d.s.c. exotherms. The heat of polymerization of the allyl group was estimated⁹ as 634.4 J g⁻¹. The DCP content was varied from 1 to 4 wt% and conversion was obtained from the exotherm peaks (Table 1). The conversion changed abruptly from 56 to 87% when the amount of initiator was varied from 1 to 2 wt%, and increased slightly above 3 wt%. Based on the results of Table 1, 4 wt% of DCP (which showed 98% conversion) was chosen as the optimum content of initiator for the remaining experiments. The conversion as a function of time (Figure 1) is almost linear up to 70% conversion for both the neat DAIP and PAr-modified DAIP. Above 70% conversion the reaction rate is reduced, probably due to the vitrification effect¹². Unmodified and modified DAIP resins showed similar cure kinetics.

Morphology

Morphological features of the various PAr-modified DAIP resins are shown in the SEM micrographs presented in Figure 2. When the PAr content is <5 phr, uniformly distributed spherical particles (<2–3 μm in size) and some particles containing DAIP inclusions are

Crack propagation



Crack propagation

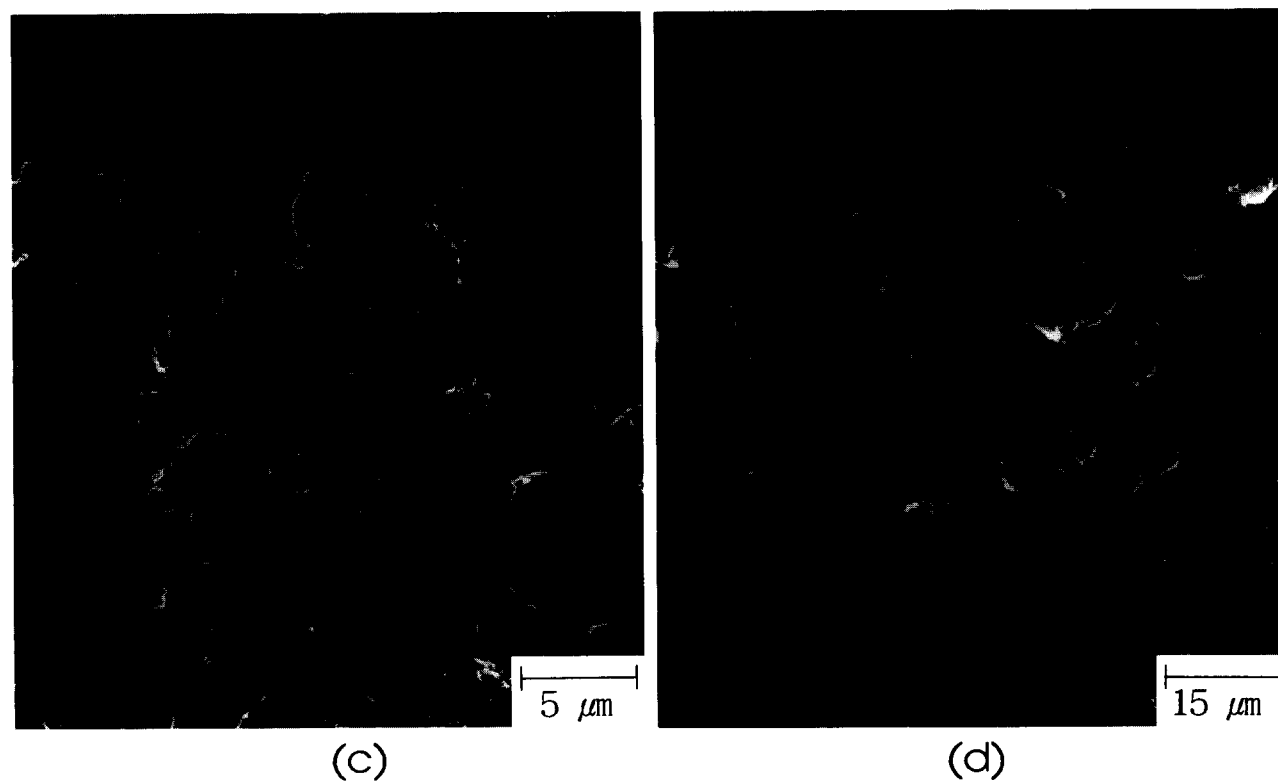


Figure 2 SEM micrographs of the fracture surfaces of DAIP/PAr alloys. PAr content: (a) 2 phr; (b) 5 phr; (c) 10 phr; (d) 15 phr

Crack propagation
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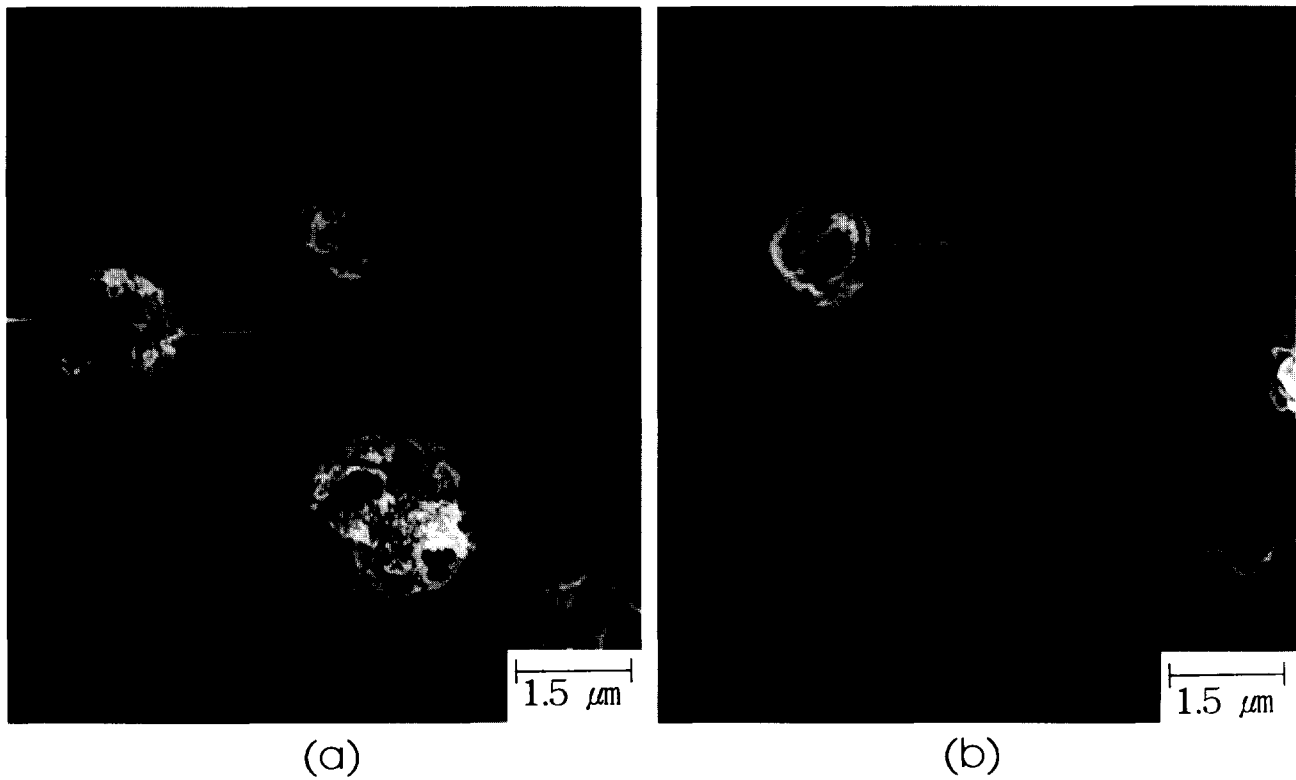


Figure 3 SEM micrographs of the fracture surfaces of DAIP/PAr alloys containing 5 phr of PAr: (a) unetched; (b) etched with methylene chloride

seen. Moreover, the shape of some particles is not spherical and some DAIP inclusions have grown out of the PAr domains and coalesced with the DAIP matrix. Comparing unetched surfaces with etched surfaces in

Figure 3, submicrometre-sized particles seen on the unetched surface that disappear after etching confirm that those particles were composed of PAr. However, some particles were composed mainly of DAIP and did

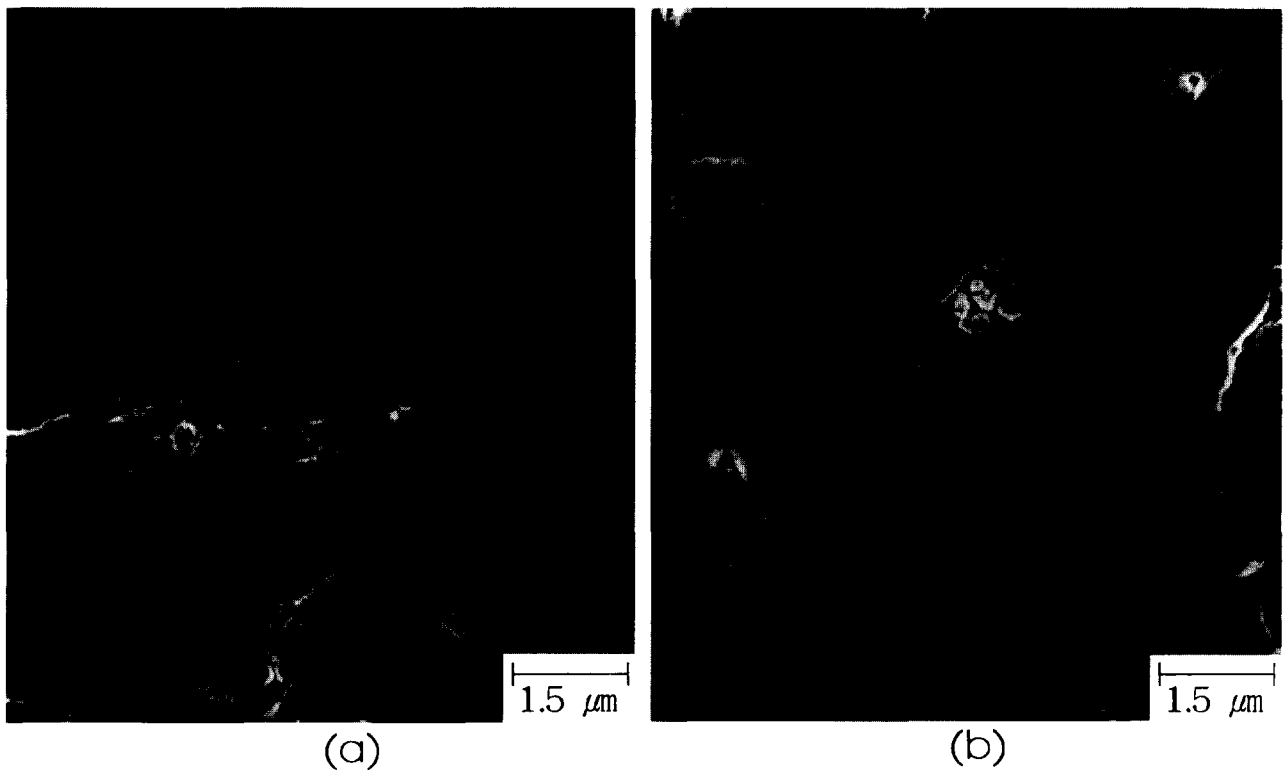


Figure 4 SEM micrographs of the fracture surfaces of DAIP/PAr alloys containing 10 phr of PAr: (a) unetched; (b) etched with methylene chloride

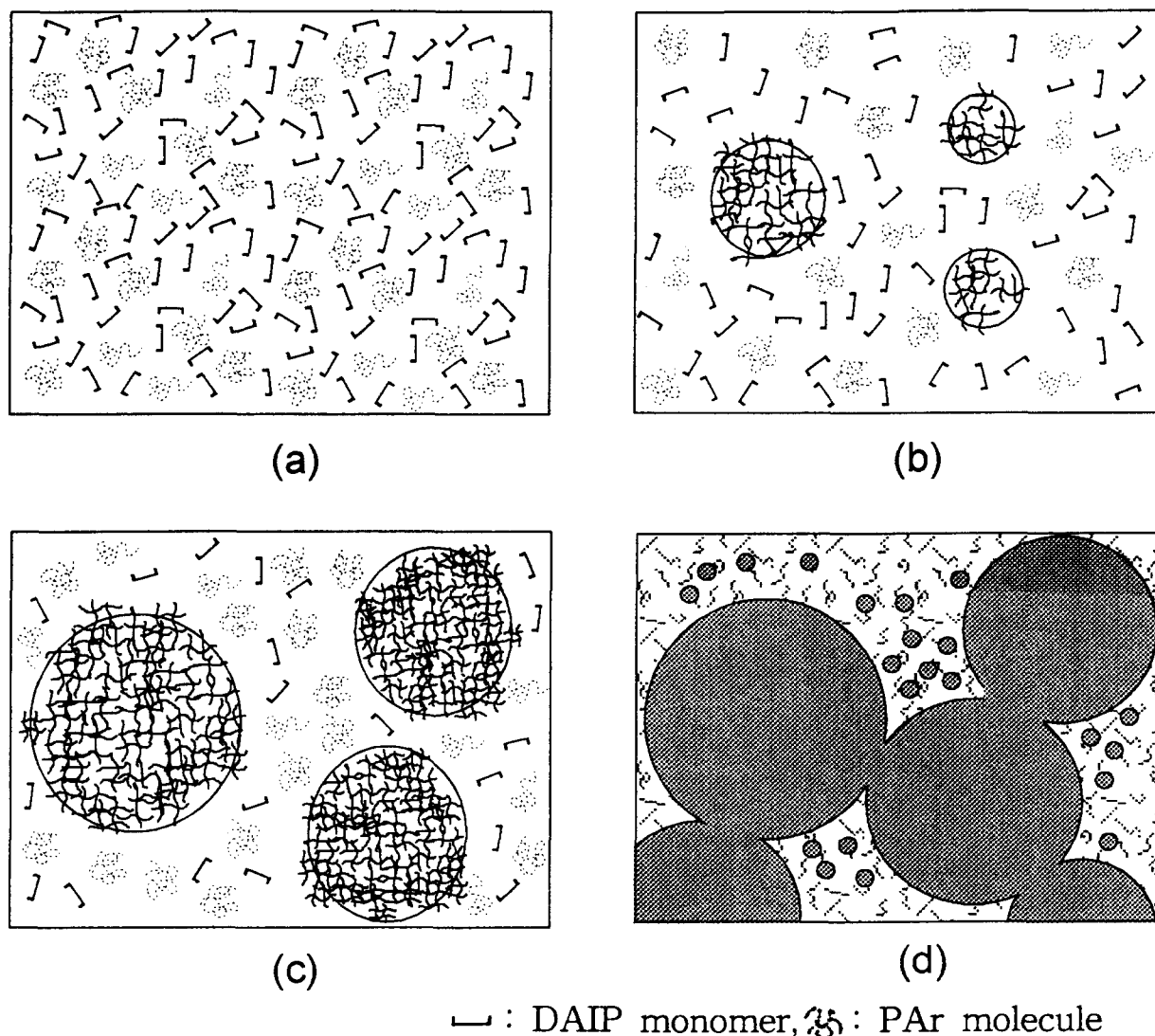


Figure 5 Schematic diagrams of the phase separation process during polymerization of DAIP for DAIP/PAr alloy: (a) homogeneous DAIP/PAr mixture; (b) formation of DAIP microgel due to intermolecular crosslinking reaction of DAIP polymer chains; (c) formation of DAIP microparticle, small amounts of DAIP monomer or oligomer are entrapped in the PAR-rich phase; (d) formation of co-continuous connected globular structure

not dissolve at all. At 10 phr of PAr, a co-continuous connected globular morphology was observed. The globules are crosslinked DAIP microparticles that have interconnected to form a continuous macronetwork. A similar morphology has been reported in the literature for thermoplastic-modified unsaturated polyester¹³ and epoxies¹⁴. The size of the globular particles is $\sim 2\text{--}3\ \mu\text{m}$ and smaller particles $\sim 0.1\text{--}0.2\ \mu\text{m}$ in size are also observed in the PAr-rich phase from etched surfaces (Figure 4). This shows that the DAIP particles have a bimodal size distribution and that the PAr is located between these bimodal sized particles to form another continuous phase. The connected globular morphology and bimodal distribution of DAIP particles are speculated to originate from microgel formation¹⁴.

Schematic diagrams of the phase separation process during polymerization of DAIP for DAIP/PAr alloy is shown in Figure 5. Before polymerization of DAIP, the reaction mixture is homogeneous. Adding an initiator and increasing the temperature starts the polymerization of DAIP, which is a free-radical chain growth reaction. As a result, from the beginning of the reaction, some high-molecular-weight DAIP polymer

chains are formed. Owing to the intermolecular crosslinking reaction of DAIP, the high-molecular-weight DAIP polymer chains immediately become highly crosslinked to form primary microgel particles at the very early stages of polymerization. The microgel formed by the intermolecular crosslinking reaction is incompatible with PAr and the PAr moves into the DAIP monomer rich phase. When this exclusion occurs the microgels are concentrated and grow in size to form larger particles, called microparticles or globules. Globules become larger by combining with other microgels or reacting with DAIP monomer supplied from the DAIP monomer rich phase containing PAr. The polymerization reaction proceeds until DAIP monomers are consumed or DAIP molecules are mobile. The microparticles grow further and finally contact with each other to yield the connected globular structure. Some of DAIP monomer becomes entrapped in the PAr phase due to the high viscosity and remains in the PAr continuous phase to form small-sized DAIP particles. As a result, the co-continuous connected globular morphology and the bimodal distribution of DAIP particles are formed.

Co-continuous morphology is also seen in the case of

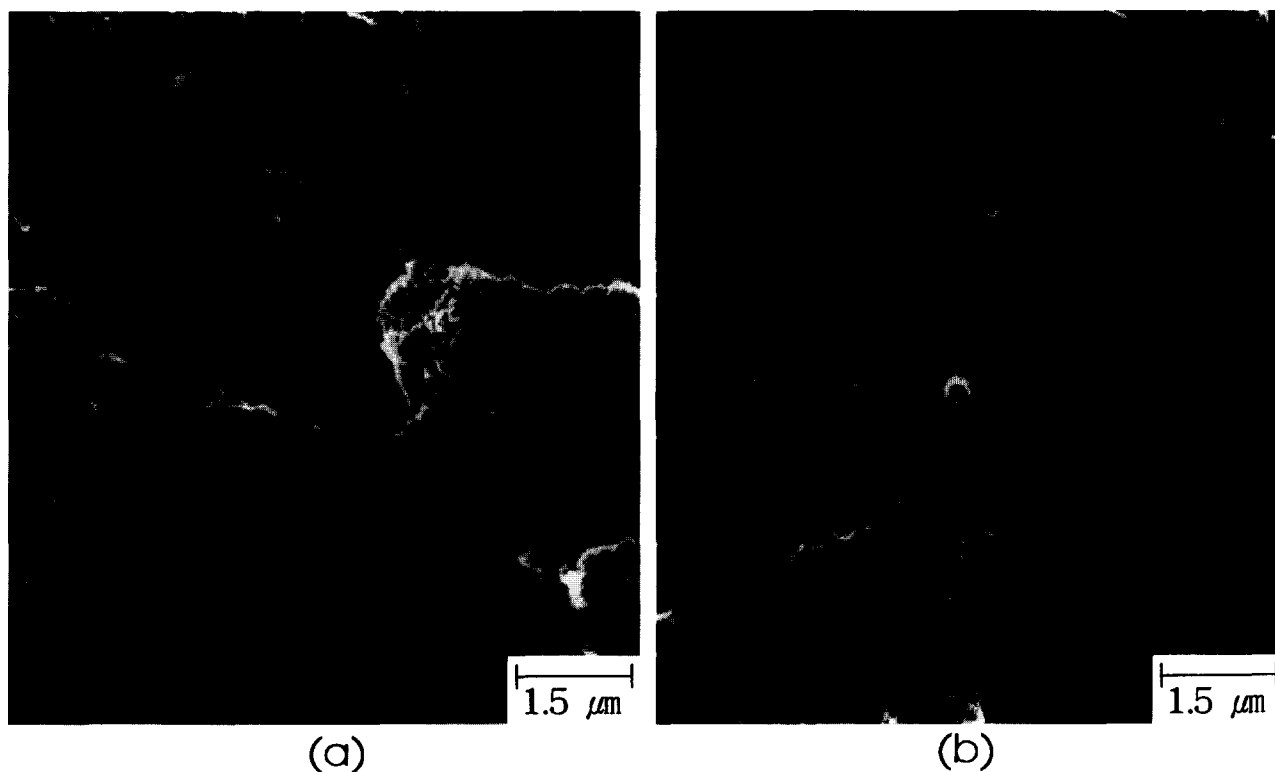


Figure 6 SEM micrographs of the fracture surfaces of DAIP/PAr alloys containing 15 phr of PAr: (a) unetched; (b) etched with methylene chloride

15 phr of PAr (Figure 6), although the fracture surfaces are very rough and the shape of the DAIP particles is irregular. Treatment of the fracture surfaces with methylene chloride reveals that the matrix mostly comprises DAIP having a flake and pore structure that connects the DAIP microparticles, while the pores are considered to be filled with PAr. The morphology of the flake and pore structure is very similar to that of other thermoplastic/thermoset blends such as unsaturated polyester resin with a high content of poly(vinyl acetate)¹³.

Dynamic mechanical spectra for the neat DAIP resin and DAIP modified with 15 phr PAr are compared in Figure 7. Because the neat DAIP resin has a very high crosslink density, it shows no glass transition temperature (T_g) and dynamic modulus decreases gradually from 270°C by degradation. The 15 phr PAr-modified DAIP resin shows a weak and broad $\tan \delta$ peak between 150 and 190°C. This gives indirect evidence for microphase separation of PAr, which cannot be observed from SEM unequivocally.

Mechanical properties

Fracture toughness (K_{IC}) results are shown in Figure 8. The fracture toughness of the neat DAIP resin was found to be 0.42 MPa m^{1/2}, indicating that the DAIP resin is quite brittle, considering the fracture toughness of tetrafunctional epoxy (0.6–0.7 MPa m^{1/2})¹⁶. The reason for this brittleness is that plastic deformation, such as crazing and shear yielding, is difficult because the molecular mobility in highly crosslinked thermosets is so restricted. The fracture toughness of the DAIP resin increased slightly on the addition of 2 and 5 phr of PAr, and formation of tails behind the spherical PAr domains (as already shown in Figure 3) of the SEM micrograph suggests that the crack pinning mechanism is operative¹⁷.

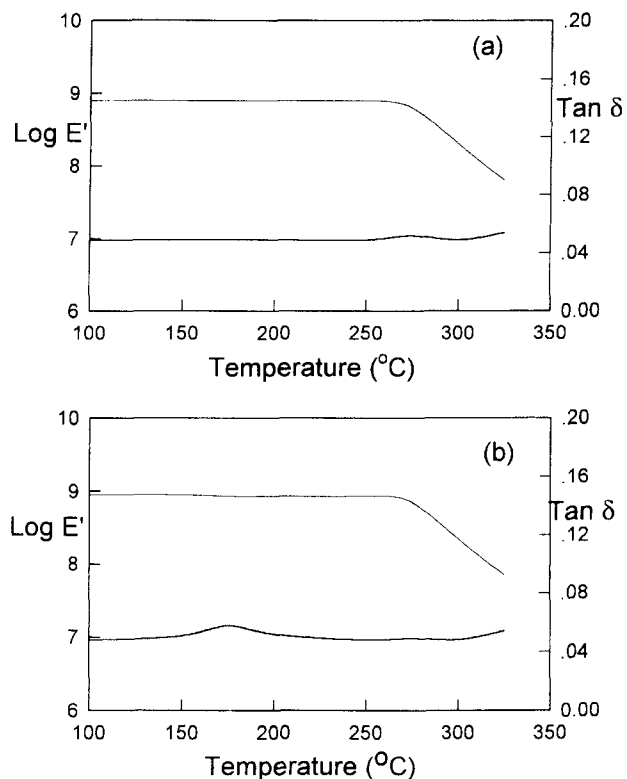


Figure 7 Dynamic mechanical spectra at 1 Hz for: (a) neat DAIP resin; (b) 15 phr PAr-modified DAIP resin

Most of the crack propagated through the particles and no plastic drawing of the particles is observed. Therefore, the amount of toughness improvement is quite small. At 10 phr of PAr, the fracture toughness increased abruptly

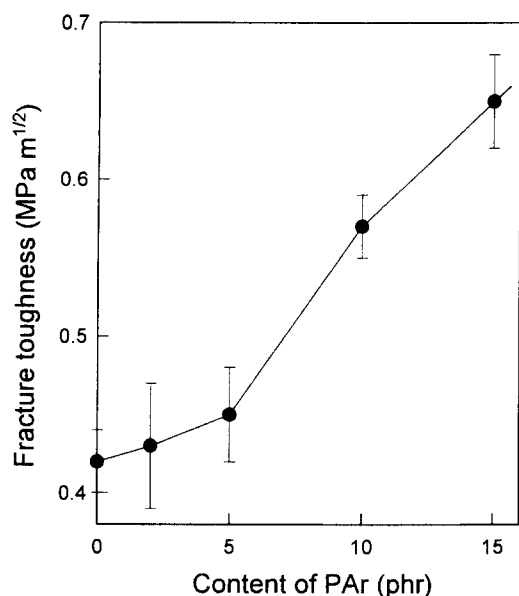


Figure 8 Fracture toughness of PAr-modified DAIP resin as a function of PAr content

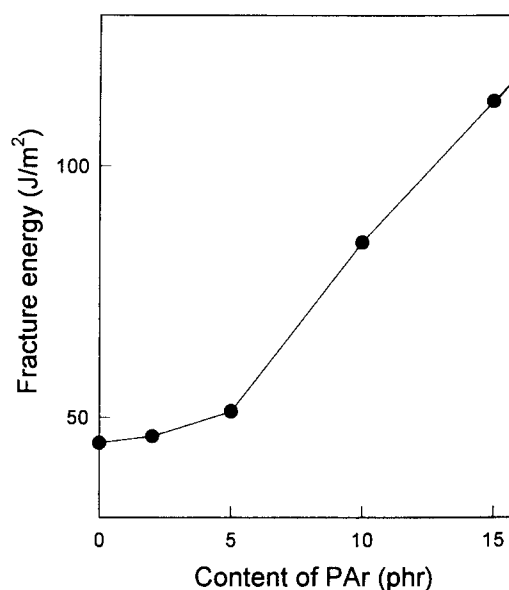


Figure 9 Fracture energy of PAr-modified DAIP resin as a function of PAr content

since the morphology undergoes a dramatic change from a particulate morphology to co-continuous globular morphology. Propagation of the main crack had some resistance, judging from the many secondary cracks that can be seen on the fracture surfaces (Figure 4). Ductile yielding of PAr located between different-sized DAIP globules was observed from SEM. The toughening effect of the PAr incorporation is illustrated more dramatically in Figure 9, in which fracture energy data are presented. The fracture energy G_{IC} is related to fracture toughness by

$$K_{IC}^2 = EG_{IC}/(1 - \nu^2) \quad (1)$$

where E is the Young's modulus and ν is the Poisson's ratio. In the case of 15 phr of PAr, a very irregular fracture surface was observed. Some of the cracks propagated through the DAIP particles, while others deviated around the DAIP particles and propagated through the matrix. Consequently, maximum ductile yielding of PAr and increased surface area by crack path deviation resulted in a 1.5 times increase of fracture toughness at 15 phr of PAr.

Flexural modulus at room temperature is plotted against content of PAr in Figure 10. Over the composition range studied, the modulus shows a slight decrease from 3.36 GPa for the neat DAIP resin to 3.14 GPa for the alloy containing 15 phr of PAr.

Figure 11 shows TOM micrographs of the neat DAIP resin taken in the plane strain region of the DN-4PB damage zone under bright field and cross-polars. No deformed region can be found near the crack tip. Under the cross-polarized light, the possible shear-yielded zone cannot be observed and the birefringent zone is assumed to be formed by the residual stress field around the crack tip. TOM micrographs taken around the crack tip of DN-4PB specimens of PAr-modified DAIP resin are shown in Figure 12. In the 15 phr PAr-modified DAIP the crack is deflected and propagates through the matrix, whereas the crack in the 10 phr PAr-modified DAIP resin is not deflected at all. This confirms that the crack deflection mechanism is operative for 15 phr PAr-modified DAIP resin.

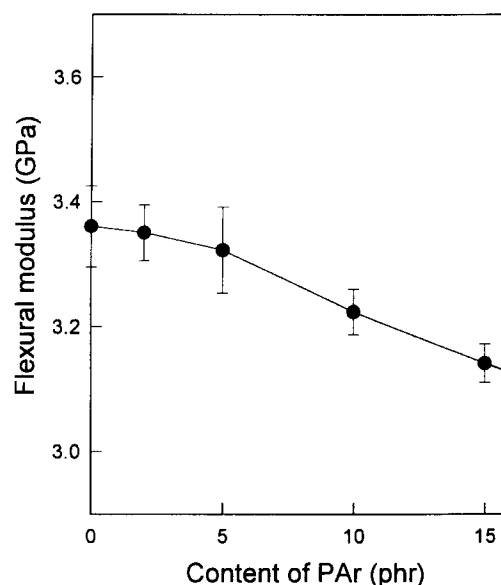


Figure 10 Flexural modulus of PAr-modified DAIP resin as a function of PAr content

DISCUSSION

Cure kinetics of thermoset/thermoplastic blends have been studied to control their morphology, which in turn determines mechanical properties. Kim *et al.*¹⁸ showed that the reaction in a blend of epoxy/poly(ether sulfone) is slower than that in the neat epoxy system and that this delay is caused by reduced mobility due to loading of the high T_g component. The delay can be also interpreted as a diluent effect; i.e. the pre-exponential factor is decreased by adding another component. In the present work, surprisingly, the cure kinetics of 15 phr PAr-modified DAIP are not significantly different from those of the neat DAIP resin.

This difference in cure kinetics is thought to result from the different phase separation process caused by the different reaction mechanism, i.e. condensation and

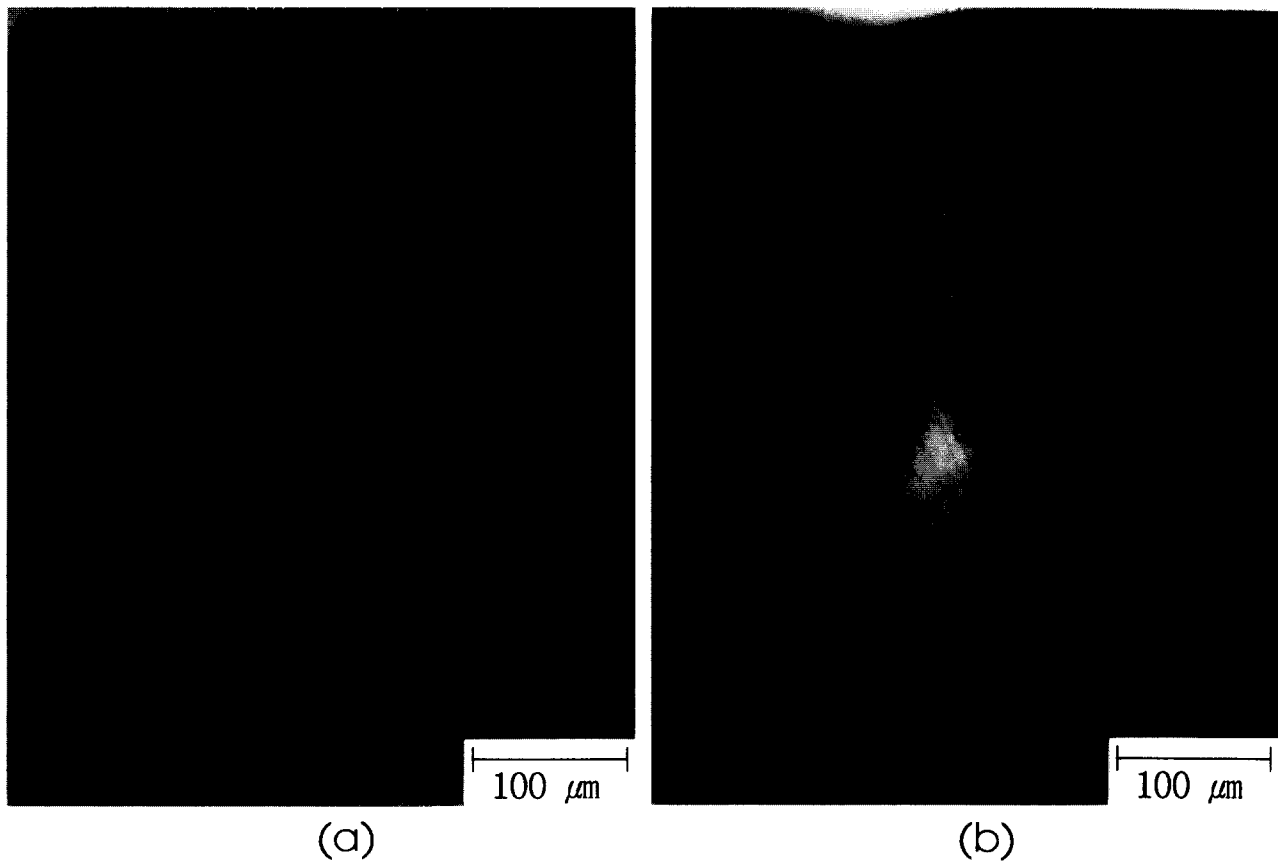


Figure 11 TOM micrographs of a thin section taken from the DN-4PB specimen of the neat DAIP: (a) bright field; (b) cross-polars

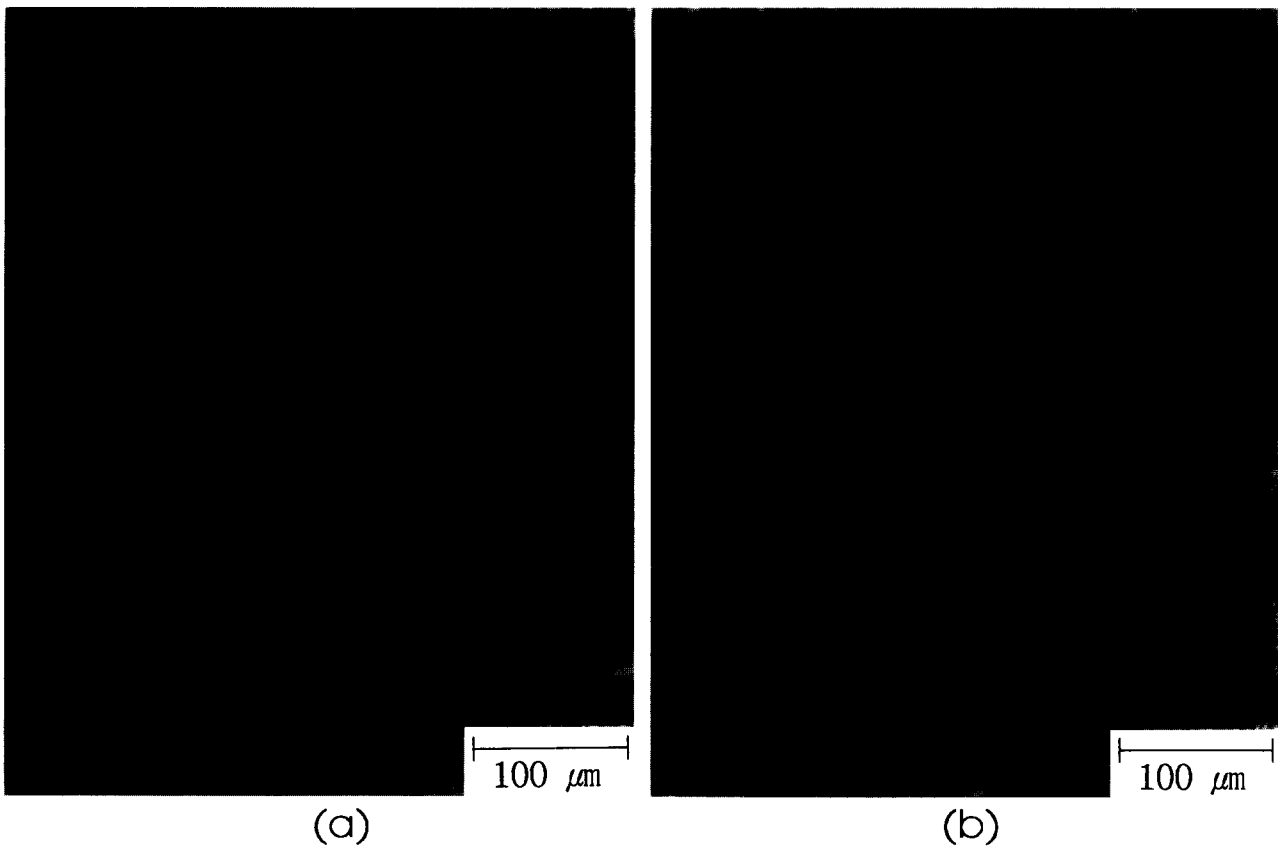


Figure 12 TOM micrographs of thin sections taken from DN-4PB specimens: (a) 10 phr PAr-modified DAIP resin; (b) 15 phr PAr-modified DAIP resin

addition reaction. In the condensation crosslinking reaction, the conversion is increased gradually by successive reactions between pairs of monomers at first and then pairs of oligomers. In this case, the effect of increasing the viscosity of the medium by adding the high T_g component is severe when the oligomer is formed, because an oligomer of moderate molecular weight does not diffuse as readily as the monomer, dimer, or trimer, etc. Therefore the addition of high T_g components increases the difference between the cure kinetics of the unmodified and modified resins.

On the other hand, in a free-radical crosslinking reaction such as the polymerization of DAIP, at the beginning of the reaction some high-molecular-weight polymer chains are formed and at the same time microgels are formed due to the intermolecular crosslinking reaction. Because PAr is not compatible with this crosslinked microgel, exclusion occurs and PAr is located in the DAIP monomer rich phase. The conversion is increased by combining concentrated microgels or by reaction with monomer diffusing from the PAr-DAIP monomer rich phase. Therefore the presence of PAr has little effect on the cure kinetics of the DAIP resin.

It has been reported^{7,8,19} that the toughness of thermoset/thermoplastic blends increases with thermoplastic content and that morphological changes do not cause step changes in the fracture behaviour of such blends. Bucknall and Gilbert⁸ suggest that the reason for this smooth change is that a single toughening mechanism operates over the whole composition range, and this appears to be a ductile drawing of the thermoplastic modifier. Kim and Brown⁷ concluded that yielding in the resin matrix was the principal mechanism of toughening when concentrations of up to 10wt% of a plastic modifier were added to a less highly crosslinked epoxy resin.

In the current study, the domains were composed of both PAr and DAIP at low content of PAr. This heterogeneity of the domain at low PAr content seemed to limit the ductile drawing of the thermoplastic phase and only caused the crack to bow out. The penetrability of the second phase determines the extent of crack bowing. Fracture surfaces show that the crack propagated through the domains, so it can be inferred that the crack pinning mechanism is not fully operative. Also, heterogeneous domains are not supposed to operate effectively as a stress concentrator to induce yielding of the matrix. Moreover, the DAIP resin used in this study is too highly crosslinked to permit yielding of the DAIP matrix, as confirmed by the DN-4PB test. Thus, the increase of fracture toughness is limited.

The step change of fracture toughness observed for 10phr PAr-modified DAIP is caused by ductile drawing of PAr. In this case, the PAr domains are completely separated from the DAIP and located between different-sized connected globules of DAIP. The toughening mechanism of 15phr PAr-modified DAIP was confirmed as ductile yielding of PAr and crack path deflection²⁰ from SEM and TOM examination (Figure 12). Deflection toughening arises when

interaction between the crack front and the minor phase produces a non-planar crack, subject to a stress intensity lower than that experienced by the corresponding planar crack. The non-planar crack arises due to the weakened matrix, which has a flake and pore structure.

Fracture toughness increased from 0.42 MPa m^{1/2} for the neat DAIP resin to 0.65 MPa m^{1/2} for 15phr PAr-modified DAIP resin. This is not as high as that obtained for the rubber-modified epoxies but still represents a respectable degree of toughening of the excessively brittle DAIP resin, particularly as it is obtained without sacrificing the modulus and high-temperature properties.

CONCLUSION

Tough PAr was used to toughen the brittle DAIP resin. The optimum initiator concentration was found to be 4wt% of dicumyl peroxide, which resulted in 98% conversion of DAIP. At low content of PAr fracture surfaces showed particulate morphology, while a co-continuous connected globular structure was obtained above 10phr of PAr. Phase separation was accompanied by microgel formation. Crack pinning was operative at low content of PAr and ductile yielding of PAr was the cause of a step increase of fracture toughness at 10phr of PAr. At 15phr of PAr, crack path deflection and ductile yielding of PAr was observed from TOM and SEM examination, and fracture toughness was increased by 1.5 times without sacrificing other mechanical properties.

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